

Review

By-Product Valorization as a Means for the Brewing Industry to Move toward a Circular Bioeconomy

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Abstract: Beer production consumes significant amounts of water, energy, and raw materials, and results in the production of various by-products, including wastewater, brewers' spent grain, yeast and hop. To lower its environmental footprint, by-products may be reclaimed or valorized in agro-food, cosmetic, material, chemical industries, etc. According to most recent research, breweries have the potential to become biorefineries, as they can extract diverse valuable plant-based compounds such as carbohydrates, proteins, lipids, phenolic compounds, platform chemicals, and biopolymers. These biomolecules possess bioactive and physicochemical properties, which can be enhanced through recovery processes. Brewery by-products may be utilized in various industries within the bioeconomy frame. In agro-food systems, extracts can increase final products' techno-functionalities. Such additives can also help in creating marketing labels such as clean-label healthy, which can further attract potential customers. Businesses can gain economic and socio-environmental benefits by implementing sustainable practices, which can also improve their corporate image. This article outlines recent advancements in the processing and valorization of brewery by-products, ultimately defining an up-to-date, sustainable strategy for clean beer production.

Keywords: antioxidant; biorefinery; application; sustainability; waste; bioactive compounds



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1. Introduction

In the future, the food supply chain is likely to come under strain due to the effects of climate change, growth in population, and the subsequent surge in demand [1]. Furthermore, humanity will have to deal with resource shortages, including water, raw materials, and energy. Thus, a more sustainable industry, taking account of the water–energy–food nexus and its scarcity dimension [2], is required to meet the needs of future generations.

Fossil-based resources are widely used in the industrial world to provide energy and chemical products. These have proven to be relatively cheap and convenient but also, as a drawback, to have significant side impacts on human health and the environment [3]. Furthermore, the depletion of fossil resources is threatening the oil-dependent global economy. In contrast to conventional linear economy, the circular economy attempts to increase the eco-effectiveness of products [4]. The environmental damage here is minimized and even a positive impact is possible. In this model, the reuse and recycling of by-products would minimize waste production and stimulate their derivation into high-value products, enhancing environmental performance and creating additional business profits [5]. As an alternative to fossil-based economy, bioeconomy is a new model based on exploiting the resources of plant origin and related products. Renewable feedstock can contribute to a lower environmental footprint, e.g., resource depletion and global warming [6]. Within the circular economy, chemicals can be extracted from agro-food waste and replace fossil-based compounds to supply the needs of the emerging bioeconomy.

Liquid and solid wastes produced by food industries, including brewing, pose both economic and environmental concerns [7,8]. Brewery solid by-products are mainly used

as animal fodder, which is a positive alternative to incineration or disposal. However, this approach does not reflect technological possibilities identified by research and the true potential of waste valorization, such as human feed, bioactive compounds recovery, bioconversion, etc. [9–11]. Regarding the wastewater produced, it is mainly treated and released into the environment, resulting in the loss of freshwater [7].

Due to the large volumes of beer produced, with a global production of 190 million m³ in 2022 [12], the brewery industry consumes large quantities of raw materials, water and energy and produces significant amounts of liquid and solid by-products. Hence, the beer industry may represent an adequate system for applying a circular bioeconomy model. Brewery by-products were extensively studied for their valorization and application in diverse industrial sectors. Figure 1 displays the number of research articles published over the years that feature solid by-products, in combination with the term “application”, and liquid by-products, along with the terms “reuse”, “biogas”, or “application”. Interestingly, the proportion of studies dealing with brewery by-products that include the application of extracts has increased more than the number of articles solely on brewery by-products.

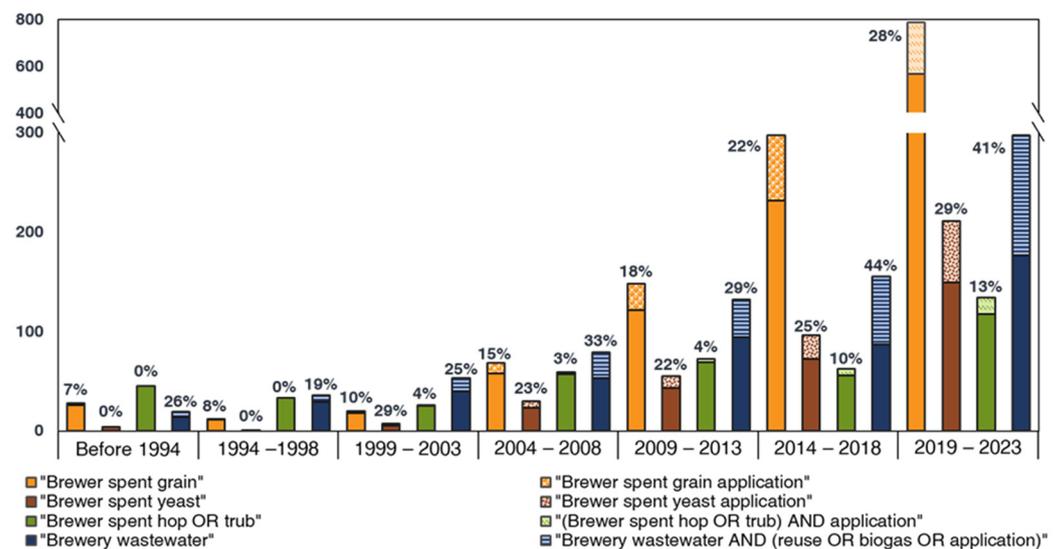


Figure 1. Evolution of the article number related to brewers’ spent grain, brewers’ spent yeast and brewers’ spent hop or trub with the proportion of the “application” term and brewery wastewater with the proportion of the “reuse”, “biogas” or “application” terms, according to the Web of Science database. The mentioned percentages indicate the proportion of articles that focus on the practical application aspect.

Some articles reviewed the brewery industry liquid and solid by-product management and valorization [13–17]. These contributions are valuable for the valorization of brewing by-products research; however, they tend to focus on specific by-products and do not take a global and systematic approach to brewing industry sustainability, e.g., beer production conservation efforts, benefits for the brewing industry and strategies for by-product valorization.

This article seeks to address these issues by exploring the potential for breweries to engage in the multi-valorization of their by-products. It summarizes the opportunity for the brewing industry to lower its environmental footprint through by-product valorization, raw material substitution, energy recovery and water reclamation. This review aims to cover the main solid by-products of the beer industry, including brewers’ spent grain (BSG), brewers’ spent yeast (BSY), and brewers’ spent hop (BSH), as well as brewery wastewater (BWW). The objective is to focus on the biomolecules extracted from specific by-products but also to provide an overview of the potential for biorefining in the brewing industry. Additionally, the benefits of implementing sustainable practices in brewing businesses are addressed.

After describing the generation of by-products from the brewing industry, the recent advances in reusing raw materials, energy and water for further beer production are detailed. The sustainability benefits of these practices for the industry are also discussed. Brewing by-products may be applied directly to other systems, yet many techniques have demonstrated their ability to extract biomolecules in a biorefinery paradigm. The impact of these processes on recovered compound properties are discussed in view of application. There are several sustainable paths and technologies available for the brewing industry. As the choice of solution may vary depending on the size of the brewery and economic background, decision-making strategies are also addressed in the manuscript. Strategies to accelerate the transition to a sustainable brewery, with potential economic and socio-environmental benefits, are also explored. Finally, a detailed scheme that outlines the paths to the valorization of brewery by-products is presented, along with recommendations for further research.

2. Raw Materials, Beer Production Process and Related By-Products

2.1. Main Constituents for Beer Production

The primary raw materials needed to brew beer are water, malt, hops and yeast. Water is used in the brewing industry not only for extracting carbohydrates from malt, but also for various requirements, such as equipment cleaning, bottle rinsing, etc. Water must be potable, free from microbiological contamination and with a controlled chemical composition. Malt is a cereal that underwent germination and thermal transformation during an operation known as malting. The cereal is first moistened to initiate germination, releasing enzymes, such as α -amylase, β -amylase and dextrinase, and then heated to develop its aromas. The temperature and duration of malting are decisive parameters for the organoleptic characteristics of beer [18]. Barley is the prominent grain used for malting. Other cereals, such as wheat and rye, can be added depending on the beer recipe. As regards the hops used, there are two types: bittering and aromatic. Bittering hops bring α -acids, responsible for beer's bitterness after the isomerization performed during wort boiling. Aromatic hops have a lower α -acid content and are richer in essential oils. In addition to their bittering and aromatic properties, hops provide phenolic compounds, which are essential for the microbiological stability of beer, and terpenes [19]. They are traditionally packaged in cones and are gradually replaced by pellets or concentrated extracts. Yeasts are unicellular organisms that transform monomeric carbohydrates into ethanol via alcoholic fermentation. Brewers' yeasts can be divided into lager-type and ale-type brewers' yeasts, fermenting at low (4–12 °C) and high (14–25 °C) temperatures, respectively. Their choice is decisive for the organoleptic properties of beer. *Saccharomyces cerevisiae* and *Saccharomyces pastorianus* yeast strains are used for ale and lager beers, respectively [20].

2.2. Beer Production and By-Product Generation

Beer is derived from plant-based materials, generating solid and liquid by-products during the process. The general scheme of beer production is shown in Figure 2. The milling stage involves malted cereal grinding. After the milling stage, starch and enzymes contained in the malt are available for extraction during the brewing process. The first step in the brewing process is the mashing stage, where milled malt is mixed with hot water, i.e., in the range of 62 to 75 °C, at a single- or multi-temperature heating stage of various durations to maximize the activation of the different enzymes responsible for the hydrolysis of starch in fermentable and non-fermentable sugars. Fermentable sugars come in monomeric form, namely glucose or fructose, or in dimeric form, such as maltose. Non-fermentable sugars, called dextrans, result from the incomplete hydrolysis of starch and are low-molecular-weight polysaccharides. Dextrans, however, contribute to beer softness [21]. During this stage, proteins are also released and will play a role in foam formation and stability. During the lautering step, beer wort is separated from the solid residue, known as BSG. During this step, BSG is rinsed with hot water to increase the recovery of fermentable and non-fermentable sugars in the beer wort. Bittering and

aromatic hops are added at the beginning and end of the boiling step, respectively. The liquid matrix is boiled until 100 °C to isomerize the α -acids, as previously mentioned, but also to promote protein coagulation, remove the volatile undesirable compounds such as aldehydes and dimethyl sulfide, and sterilize the beer wort. After boiling, the whirlpool step separates the wort from the solid residues, i.e., trub and BSH. Yeasts carry out alcoholic fermentation. The *Saccharomyces* species are mainly used in the industry [22]. Yeast type, temperature and fermentation time are decisive parameters for the organoleptic characteristics of the finished product. Primary fermentation, where ethanol and carbon dioxide are produced, lasts from 2 to 10 days, after which beer is transferred to low-temperature storage tanks for one to several weeks to finish fermentation and refine the beer. The yeast is cropped from fermenters after the end of fermentation. Several technologies are available to remove residual yeasts and suspended solids, including centrifugation, frontal filtration performance with diatomaceous earth, or tangential filtration. Fermented beer includes compounds that can make it naturally cloudy [23]. Unlike in craft microbreweries and most beer styles, turbidity is undesirable for marketing reasons in the brewing industry. After removing suspended solids and yeasts, a colloidal stabilization step can also be carried out, for instance, with polyvinylpyrrolidone filters. Conditioning is the final production step and produces wastewater and solid wastes, such as glass bottles, labels, and metal products. All production steps produce BWW.

Beer production is extensively water consumptive, with a water-to-beer ratio mid-percentile of 2.79–4.11 L·L_{beer}⁻¹ in 2020 [24]. According to the most recent environmental, social and governance report of the Carlsberg group, for a water use to beer ratio of 2.53 L·L_{beer}⁻¹, the breweries produced 144 g·L_{beer}⁻¹ of solid waste and by-products and 1.45 L·L_{beer}⁻¹ of wastewater in 2022 [25].

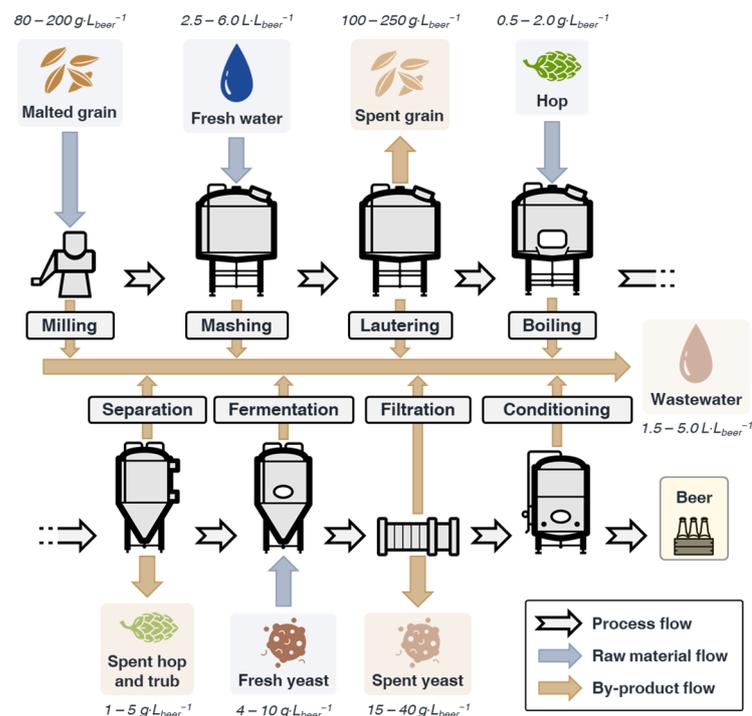


Figure 2. General processing of beer production with consumed raw materials, generated by-products and associated mass balance [25–27].

3. Resource Conservation: Closing the Loop

The release of by-products can have a significant impact on the environment, which, in turn, represents a cost for industries. One of the ways to deal with this issue is to reduce the amount of waste generated. Moreover, the increasing demand for raw materials, water,

and energy has a negative impact on the environment and is threatening the resilience of the food supply system. In this context, one potential solution is to reclaim waste streams from breweries either in the manufacturing process or by treating them to generate energy, which promotes sustainability.

3.1. Raw Materials Substitution or Reuse

Yeast is an easy-to-reclaim waste. At the end of fermentation, BSY cells are harvested and added to the next ferment [28]. This process is called repitching. However, yeast performances seem to deteriorate with repitching. Therefore, serial repitching affects cell viability, physiology and oxidation, thus affecting fermentation performances and beer quality [29]. Performance loss is likely higher in the case of *S. cerevisiae* compared to *S. pastorianus*. This was recently explained with cell-wall modification induced by repitching stress; unlike *S. cerevisiae*, *S. pastorianus* can create a resistant cell-wall structure composed of β 1,4- and α 1,4-Glucan linkages [30]. This practice reduces yeast brewery needs.

BSG carbohydrate composition is likely too low for direct reuse for the next mashing batch. However, malted grain consumption may be lowered using substitute material, as shown in Figure 3. One of the most promising materials is bread residue. According to a recent study, up to 50% of malt may be replaced by bread with similar physicochemical properties of ale beer compared to the control, a 100% malt ale beer. Furthermore, the whole wheat bread displayed higher antioxidant capacity, phenolic compounds concentration and better organoleptic sensorial characteristics than the control [31]. Replacing malt with bread has also been tested with lager beer. A small adjunct of residue bread, i.e., up to 30% of the malt ratio, showed higher organoleptic ratings than the control, whereas a ratio higher than 30% showed lower ratings, with some taste flaws as salt, yeast and diacetyl feelings [32]. Using bread surplus can reduce breweries' malt consumption and improve the environmental performance of classic bread waste treatment systems, mainly incineration, anaerobic digestion (AD) or disposal [33]. A life cycle analysis showed that using surplus bread in brewing may save $0.46 \text{ kgCO}_2\text{eq} \cdot \text{kg}_{\text{bread}}^{-1}$ emission in the global warming category. Replacing malt with bread had an environmental savings score, which was calculated considering all environmental factors, of -24 mPt per kg of bread. This score was lower than the savings achieved through source reduction (-49), animal feed (-30), and donation (-28). However, it was higher than the savings from ethanol production (-17), incineration (-3), and AD (0) [34]. Some fruits could also be used as a carbohydrates source due to their high fermentable sugar content, such as cocoa [35].

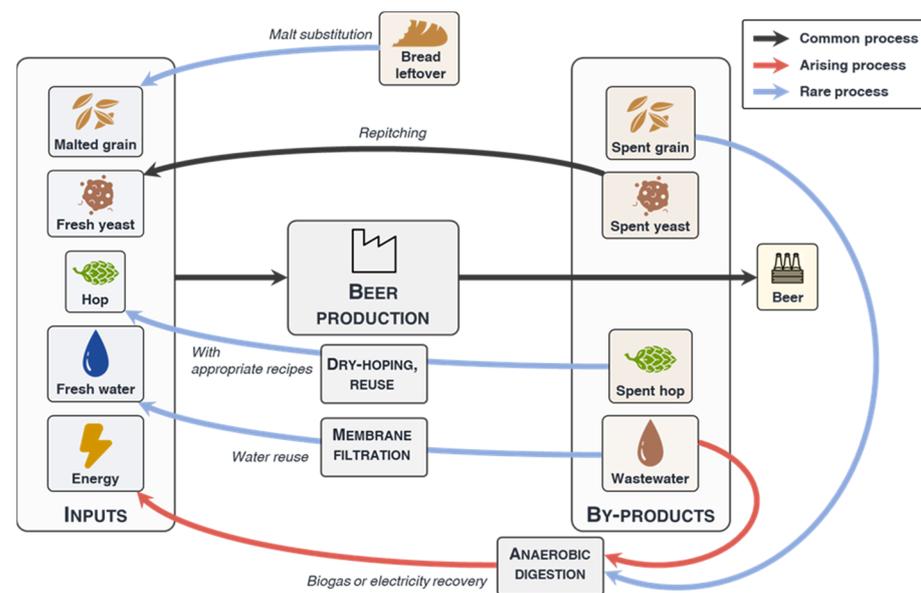


Figure 3. By-product recovery to mitigate brewery raw materials, water and energy consumption.

Dry hopping is a technique that has gained popularity over the last years. In contrast to addition at the end of the boiling step, dry hopping is a cold extraction of hop at the end of fermentation or during maturation. This technique improves aroma-related compounds extraction, but also the oxidative stability of beer [36,37], making it a valuable tool for breweries to increase resource conservation, e.g., enhancing the efficiency in the use of hops. Hop pellets used for dry hopping may be reused for further hopping. Gasinski and co-workers showed that beers with a hop from a previous dry hopping process contained lower concentrations of some volatile compounds such as aromadendrene, α -terpineol, methyl geranate, and α -caryophyllene, but similar total volatile compounds, phenolics compound concentration, and antioxidant capacity, compared to the control, composed of fresh hop pellets. In addition, panelists described beer with recycled hops as tasting better [38]. Optimization of dry hopping was also reported with several extraction techniques. For instance, supercritical CO₂ extraction reduces energy and solvent consumption during hop extract production [39]. Alternatively, fractional condensation under vacuum allowed hop amount and energy consumption reduction. Several fractions with different volatile profiles were obtained, proving the versatility of this technology [40].

3.2. Energy Recovery

Energy, in biogas or in electricity form, can be recovered from solid and liquid residue matrices (Figure 3). Solid by-products, such as BSG and BSY, can be processed through AD to produce methane (CH₄), hydrogen (H₂), or a mix of these two gases, called biohythane. Hydrogen production may be realized either with dark fermentation [41] or photo-fermentation [42]. Fermentation process parameters, such as pH, culture type or time, must be carefully optimized, as they influence biogas production and composition, as well as by-products generation [43]. The optimization of operating conditions may be performed with the help of statistical tools. For example, central composite design and response surface methodology were successfully achieved in the AD of BSG, resulting in optimal temperature (35 °C) and substrate concentration (18 g_{BSG}·L⁻¹) determination [44]. This energy flux can be sold to generate extra revenues or used directly on a brewery plant to lower its consumption. Sganzerla and co-workers optimized dry BSG in AD to produce methane, and obtained a yield of 10.53 L_{CH₄}·kg_{total volatile solids}⁻¹. According to the latter results, purified methane could generate electric and thermal energies in industrial heat and power unit, which covers 7.38 and 6.86% of the electricity and heat required for beer production, respectively. Thus, breweries may reduce their energy consumption and mitigate greenhouse gas through the AD of by-products [45]. Other brewery high-organic-load by-products were tested for methane production with AD, such as whirlpool residue and end-of-fermentation beer [46]. Results showed that BSG and BSY, with the addition of biochar and granular activated carbon, yielded 486.9 L_{CH₄}·kg_{volatile solids added}⁻¹, and spent grain, up to 356.2 L_{CH₄}·kg_{volatile solids added}⁻¹, respectively. The co-digestion of 70% BSY and 30% BSG was tested and produced 447.7 L_{CH₄}·kg_{volatile solids added}⁻¹ with a synergistic effect. With such productivity performance, this process would cover, respectively, 53.9 and 64.4% of the electric and thermal consumption of the brewery [46]. Second-generation ethanol can be produced through micro-aerobic or anaerobic fermentation. Carbohydrates can be released through acid hydrolysis with an average yield of 81–94% and ethanol production of 0.227–0.251 L_{ethanol}·kg_{BSG}⁻¹ [47–49]. Other pretreatments exist, such as subcritical water, enzymatic hydrolysis, etc. Subcritical water resulted in higher productivity and a lower amount of ethanol, namely 0.067–0.87 L_{ethanol}·kg_{BSG}⁻¹ [50]. Biofuel production through algal cultivation and pyrolysis from BWW was also reported [51].

Most BWW is treated on-site with aerobic biological treatment and rejected to lakes or rivers. BWW is mostly treated with aerated sludge processes, consuming a large quantity of energy because of aeration [52]. Biogas production was also reported during BWW AD treatment. This practice is emerging at an industrial scale, with 18 out of 84 sites in the Carlsberg group [25]. Performances may be optimized with innovative processes such as utilizing low voltage during fermentation. Adding 0.10 V appears to improve

the performance of anaerobic digestion by increasing the conductivity of the sludge and extracellular polymeric substances of cells, resulting in enhanced organic load degradation and methane production [53]. The co-digestion of BWW and BSG for hydrogen production was recently tested. A hydrogen productivity decrease was observed when 17.5% of BSG was added to the matrix. This result was explained by the increase in nitrogen content, which promoted ammonia inhibition [41]. This increase in nitrogen was also observed during BSY and BSG co-digestion [46]. Apart from biogas production with AD, another promising technique for low-energy sustainable wastewater treatment is microbial fuel cell (MFC). This system uses microorganisms to degrade organic load while generating electrical current and has gained attention in the last decades for real wastewater treatment [54]. MFC was applied to BWW treatment, with chemical oxygen demand, total dissolved solids, total nitrogen and total phosphorous removal of 79–87, 76–78, 66 and 75%, respectively [55,56]. Other works obtained similar chemical oxygen demand removal performances during a one-year run. The techno-economic assessment was realized, and the cost of the studied system was two orders lower than conventional activated sludge systems. Authors suggested upcoming research developments such as higher flow rate study, low-cost cathodic catalyst material or MFC connection in parallel or series [57]. The energy consumption of MFC systems was 3 to 10 times lower than that of conventional aerobic treatment systems [56,57]. According to a recent study, algal biomass may also treat BWW with reduced energy consumption, up to 3-fold less [52]. In addition, algal processes may allow for nutrient recovery, as discussed in Section 5.

3.3. Water Reclamation

Water reuse was performed for years in some breweries (Figure 3). Multiple pieces of research focus on BWW treatment performance maximization with novel techniques, yet few studies really consider water reuse in their process. The most promising techniques are the coupling of anaerobic membrane bioreactor (AnMBR) and cross-flow filtration processes, whose most classical technologies are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) or reverse osmosis (RO), or the coupling of techniques. AnMBR-treated-BWW processing with direct contact membrane distillation, NF and RO were compared for water reclamation. RO and membrane distillation showed similar total organic carbon, chemical oxygen demand, total nitrogen and total phosphorous rejection. Membrane distillation performed an 86% recovery of high-quality water [58]. Biologically treated BWW has also been processed with ozone/coagulation/MF/RO or UF/RO. As a result, the MF and UF permeate complied with the requirements for industrial reuse, and RO permeate met the requirement of national drinking water regulation [59]. As 30% of brewery water is used for operations without product contact, wastewater may be recycled with industrial use quality [60]. Verhuelsdonk and co-workers studied AnMBR/UF/RO system performances with an economic study [61]. A combination of these technologies allowed for the production of drinking water in compliance with the set of drinking water requirements, with a recovery yield of 63.3%. These performances were obtained at a pilot scale on a process operating for two years at a flow rate of 0.5–1.0 m³·h⁻¹. The techno-economic assessment was realized with a Monte-Carlo analysis with varying operating parameters, i.e., membrane lifespan, RO recovery, and electrical energy, wastewater disposal, freshwater and sludge disposal costs. Hence, 77.2% of the cases resulted in the economic viability of the studied process, with a positive median value of 0.61 €·m⁻³ [61]. Techno-economic analysis of a wastewater reuse project can be realized by brewing industries with its own cost with such studies.

4. Direct Applications of Brewery By-Products

4.1. Current Use of Brewery By-Products

Among the by-products of the brewing industry, a large part is used for animal feed. According to Carlsberg group figures, in 2022, approximately 83% of the total solid waste consisted of BSG and BSY, with 97% used as animal fodder and 3% as fertilizer [17].

Those practices seem to have environmental and economic benefits that could be increased with human consumption [26]. The current use of brewery solid wastes as animal feed does not reflect the technical possibilities of the more valuable valorization of these by-products [51]. Similarly, BWW contains bioactive compounds that enable alternative methods of valorization with greater value [62]. To understand brewers' waste management practices, 11 craft brewery businesses were surveyed in Brazil. BWW was mainly treated and rejected. Ten out of 11 brewers utilized their solid waste for the agricultural sector, and more interestingly, 4 out of 11 were not aware of alternative routes apart from using it as animal feed [63]. Besides misinformation, the motivation of producers to embrace sustainable approaches was identified as another factor limiting the emergence of a green industry. Due to the various business and financial challenges that are inherent in the beer-specific economic context, brewers seem to be facing difficulties in finding the motivation to embrace environmentally friendly practices [64]. Thus, the brewing sector would benefit from exploring more valuable ways to valorize its waste. Alternative paths to current brewing by-products' end of life, with innovative direct application and without major modification, were recently investigated by researchers.

4.2. Solid By-Products

BSY is used as animal feed due to its high protein content or as flavoring products and in human food products [65]. BSY possesses several physicochemical properties enabling applications outside conventional valorization research fields, as displayed in Figure 4. For instance, the BSY surface was characterized as "spindle and pointed egg-shaped", promoting the organic and inorganic pollutants adsorption from wastewater. As a result, BSY was used as a biosorbent of Remazol Red F3B [66]. Another group successfully realized the adsorption of another textile dye, Congo Red, with BSY. The use of ultrasound in the desorption process yielded a 100% dye desorption with NaOH as the desorption solvent [67]. Besides textile dye, brewery sludge was used for the removal of metal compounds from wastewater [68]. Likewise, Zeolite was functionalized with spent yeast from a microbrewery to recover platinum group metals from an aqueous solution. Authors showed that operating parameters, such as flow rate, pH and column height, allowed different adsorption behaviors, and thus, different performances in the separation and recovery of Pd(III), Ir(III) and Rh(III) [69].

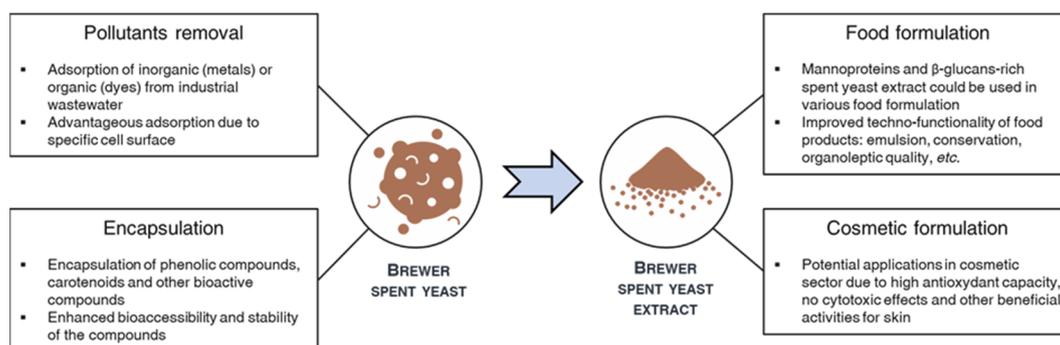


Figure 4. Novel applications of brewers' spent yeast and brewers' spent yeast extract.

Another application of BSY is valorization as carrier material to encapsulate bioactive compounds, like carotenoids from pumpkin peel extract [70] or curcumin [71]. Encapsulation increased compounds' stability and enhanced bioaccessibility with gradual release during simulated gastrointestinal digestion [70]. BSY cell wall components such as β -glucans and mannoproteins were the main compounds which encapsulated compounds interacted with [71]. Brewery by-products can be used as feed for insect farming, an alternative to cattle fodder. Brewery solid waste was investigated as black soldier fly larvae feed, compared to chicken feed. The authors concluded that the solid waste that was examined showed similar characteristics to other starch-rich materials in terms of

how insects metabolize them [72]. This suggests that brewing by-products could be a viable option for producing insect-based proteins, which could potentially help address environmental challenges related to food production [73]. Brewery by-products were also studied for raw materials substitution. In this framework, BSG use in formulation may add nutritional values to noodles [74], candies [75], etc.

4.3. Brewery Wastewater

As described in Section 3, a major part of treated BWW is rejected in the environment. Closing the water cycle with recycling and reuse is in accordance with the third target of the United Nations Sustainable Development Goal 6, clean water and sanitation. Water reclamation in brewery plants has been discussed earlier; nonetheless, recycling can be achieved in other sectors, especially the agricultural sector. Indeed, AD-treated BWW demonstrated fertilizing action on mustard greens, basil and lettuce crops [76]. Alayu and co-workers investigated irrigation effects on tomato cultivation with two BWWs: AD-treated BWW with and without additional constructed wetland treatment [77]. Both treated wastewaters affected tomato growth, i.e., plant height, number of leaves, biomass and fruit yield. These findings suggest that brewery output water stream may bring nutrients and water to agricultural fields, a process called fertigation. Fertigation reduces both synthetic fertilizers and freshwater needs. However, soil irrigated with AD-treated BWW showed an increase in pH and exchangeable cation (Ca^{2+} , Mg^{2+} , K^{+} and Na^{+}) concentration. This negative impact was lowered with additional constructed wetland treatment [77]. In another study, soil modification was linked to a high salt concentration, or conductivity of around $3\text{--}4\text{ mS}\cdot\text{cm}^{-1}$ [78]. To mitigate this negative impact, *Beta vulgaris*, a salt-tolerant crop, and *Trichoderma asperellum*, a fungus, were respectively used as cultivation species and as soil amendments. This strategy decreased BWW impact on most salt accumulation on soil, but to a lesser extent for Na^{+} [78].

By-products may be valorized in various fields. Functionality brought by brewery by-products is often correlated to their organic content, i.e., carbohydrates, proteins, phenolic compounds, etc. Hence, to suit their potential application framework even more, valuable biomolecules from brewery by-products may be extracted, selected and modulated with various processes in a biorefinery paradigm, as discussed in Section 5.

5. Brewery as Biorefinery

Brewery by-products, i.e., BSG, BSY, BSH and BWW, are a great source of biomolecules, such as carbohydrates, lipids, proteins, lignin, etc. and other bioactive compounds, such as phenolic compounds. The chemical composition differs for each by-product and is depicted in Figure 5. Adequate extraction technologies allow for the recovery of targeted biomolecules that can be used in various applications in food and biotechnology. Recently, novel approaches have emerged where the extraction process may eventually be used to modify the properties of the extract to suit specific applications better.

A literature survey has been carried out on bioactive compounds and biopolymers recovery from brewery waste streams, and the most recent advances are summarized in Table 1.

Table 1. Recent advances in brewery by-product processing with the aim of biomolecules or biopolymers recovery.

By-Product	Target Compounds	Method	Operating Conditions	Outcome	Reference
BSG	Carbohydrates	Fungal solid-state fermentation, ionic liquid extraction and enzymatic hydrolysis	Fermentation: 30 °C; 1×10^6 g _{spore} ·g _{BSG} ⁻¹ of <i>Aspergillus brasiliensis</i> ; 5 d Extraction: 90 °C; 10 g of cholinium glycinate; 16 h Enzymatic hydrolysis: 50 °C; 160 rpm; 4 h	24.12 ± 2.07 glucan, 54.37 ± 2.34 xylan and 57.04 ± 2.22% arabinan recovery yield Ionic liquid recovery with similar performances up to 5 cycles	[82]
BSG	Carbohydrates	Ionic liquid extraction	Extraction: 90 °C; 120 rpm; 5:100 BSG:IL (<i>w:w</i>) with cholinium glycinate ionic liquid; 16 h Antisolvent extraction: room temperature; 1:1 acetone:water (<i>v:v</i>); 30 min + centrifugation at 2755 × g; 30 min + filtration 0.45 µm	71% delignification with high glucan, xylan and arabinan recovery	[83]
BSG	Enzymes	Fungal solid-state fermentation	Fermentation: 25 °C; 75% relative humidity; 2×10^6 spore inoculate; 7 d Extraction: 1:5 BSG:water (<i>w:v</i>)	<i>Aspergillus ibericus</i> : 300–313 U _{xylanase} ·g _{dryBSG} ⁻¹ and 51–62 U _{cellulase} ·g _{dryBSG} ⁻¹ <i>Aspergillus niger</i> CECT2088: 94 ± 4 U _{β-glucosidase} ·g _{dryBSG} ⁻¹	[84]
BSG	Enzymes	Fungal solid-state fermentation	Pretreatment: 121 °C; 1% NaOH:water (<i>w:v</i>); 1 h + 98–100 °C in water; 1 h Fermentation: 30 °C; 80% relative humidity; 5×10^6 spore inoculate of <i>A. niger</i> CECT2070; 7 d Extraction: 1:10 BSG:water (<i>w:v</i>) with 50 mmol·L ⁻¹ citrate buffer at pH 4.8	1400.8 U _{xylanase} ·g _{dryBSG} ⁻¹ and 6.23 U _{cellulase} ·g _{dryBSG} ⁻¹	[10]
BSG	Lignin	Deep eutectic solvent extraction	120 °C; 5:1 lactic acid: choline chloride (<i>mol:mol</i>); 5 h	Lignin extraction yield of 54.4 ± 2.6% with >75% purity	[85]
BSG	Lignin	Deep eutectic solvent extraction	80 °C; 1:20 biomass:DES (<i>m:m</i>); 1:10 choline chloride:lactic acid (<i>mol:mol</i>); 24 h	Lignin extraction yield of 39.3% with 53% of β-O-4 inter-unit bonds	[86]
BSG	Lignin and carbohydrates	Organosolv extraction and centrifugation	Organosolv pretreatment: 180 °C; 1:1 ethanol:water (<i>v:v</i>); 120 min Centrifugation: 4500 × g; 5 min	Lignin fraction: 95% (<i>w:w</i>) with 58% yield Glucan (cellulose) fraction: 39% (<i>w:w</i>) with 60% yield	[87]

Table 1. Cont.

By-Product	Target Compounds	Method	Operating Conditions	Outcome	Reference
BSG	Phenolic compounds	Acid pretreatment and alkaline hydrolysis	Acid pretreatment: 120 °C; 0.2% sulfuric acid; 17 min Alkaline hydrolysis: 120 °C; 1:20 BSG:NaOH solution (<i>w:v</i>); 2% NaOH (<i>w:v</i>); 90 min Extraction: 35.4% HCl addition; 80% ethanol addition and evaporation	1.185 mg _{GAE} · g _{dryBSG} ⁻¹ including 0.46 mg · g _{dryBSG} ⁻¹ of ferulic acid extract	[88]
BSG	Phenolic compounds	Microwave assisted extraction	Microwave pretreatment: 600 W; 30 min Extraction: 80 °C; 1:30 BSG:solvent (<i>w:v</i>); 70:30 ethanol:water (<i>v:v</i>); 60 min	13.23 mg _{ferulicacidequivalent} · g _{dryBSG} ⁻¹ extract rich in ferulic and p-Coumaric acids	[89]
BSG	Phenolic compounds and proteins	Ultrasound assisted extraction	47 °C; 20 kHz; 21.7 mL _{water} · g _{BSG} ⁻¹ ; pulse mode (5 s/5 s); 0.5 h	Phenolic compounds: 3.28 ± 0.12 mg _{GAE} · g _{dryBSG} ⁻¹ Proteins: 82 ± 1 mg _{protein} · g _{dryBSG} ⁻¹	[50]
BSG	Phenolic compounds, fatty acids and nitrogen compounds	Pyrolysis	25–700 °C; 1, 2 and 4 °C · min ⁻¹ heating rate; 50 mL · min ⁻¹ nitrogen flow	13.94% phenolic compounds, 23.95% fatty acids and 25.10% nitrogen-compounds release	[90]
BSG	Platform chemical—2,3-Butanediol	Bacterial bioproduction	Pretreatment: 400 W; 10% BSG:water (<i>w:v</i>); 0.5% NaOH:water (<i>v:v</i>); 60 s Enzymatic hydrolysis: pH 6.0; 50 °C; 10% BSG:water (<i>w:v</i>); 2% enzyme:water (<i>v:v</i>) Culture: 30 °C; 180 rpm; <i>Enterobacter ludwigii</i> mutant strain inoculate; 12 h	batch: 16.4 g _{BDO} · L ⁻¹ with 0.41 g _{BDO} · g _{glucose} ⁻¹ fed-batch: 118.5 g _{BDO} · L ⁻¹ with 0.43 g _{BDO} · g _{glucose} ⁻¹	[91]
BSG	Platform chemical—5-hydroxymethylfurfural	Subcritical water hydrolysis and liquid-liquid extraction	Subcritical water hydrolysis: 180 °C; 15 MPa; 22.5 g _{water} · g _{BSG} ⁻¹ ; 5 mL · min ⁻¹ water flow Liquid-liquid extraction: pH 6.5; 35 °C; 1:2 hydrolysate:ethyl acetate (<i>v:v</i>)	73.85% of dry BSG 5-hydroxymethylfurfural recovery	[92]
BSG	Platform chemical—itaconate	Fugal bioconversion	Hydrolysis pretreatment: 180 °C; 600 rpm; 1:8 BSG:water (<i>w:v</i>); 15 min Enzymatic hydrolysis: pH 7.5; 50 °C; 70 g _{dry matter} · L ⁻¹ BSG:water (<i>w:v</i>); 25 rpm; 72 h Culture: pH 6.5; 30 °C; engineered <i>Ustilago maydis</i> ; 120 rpm	0.38 g · g _{carbohydrates} ⁻¹ itaconate productivity with 0.11 g · L ⁻¹ · h ⁻¹ yield	[93]

Table 1. Cont.

By-Product	Target Compounds	Method	Operating Conditions	Outcome	Reference
BSG	Platform chemical—VFAs	Fermentation	pH 9.0; 35 °C; 1:5 anaerobic sludge:BSG (volatile solids:volatile solids) inoculate; 10 d	9258 mg _{VFA} ·L ⁻¹ with high acetic and butyric acids content	[43]
BSG	Platform chemical—Lactic acid	Simultaneous saccharification and fermentation	pH 5.5; 37 °C; 100 rpm; <i>Lactobacillus pentosus</i> TISTR 920 inoculate; cellulase and xylanase enzyme cocktail converted from BSG; 72 h	59.3 ± 1.0 g·L ⁻¹ lactic acid production with 0.297 g·g _{BSG} ⁻¹ yield	[94]
BSG	Polyhydroxyalkanoates or related biopolymer	Bacterial bioproduction	50.12 g _{BSG} ·L ⁻¹ ; 0.22 g _{yeast extract} ·L ⁻¹ ; 24.06% (v:v) salt concentration; <i>Bacillus sphaericus</i> NCIM 2478 inoculate	916.31 mg·L ⁻¹ of PHB	[95]
BSG	Polyhydroxyalkanoates or related biopolymer	Bacterial bioproduction	pH 8.0–8.8; room temperature; microbial mixed culture enriched with PHA accumulating organisms	35.2 ± 5.5% (w:w) of PHA accumulated	[96]
BSG	Proteins	Alkaline extraction	pH 11.0; 60 °C; 1:17 BSG:water (w:v); 3 h with sequential centrifugation	87% protein yield	[97]
BSG	Proteins and platform chemical—VFAs	Alkaline pretreatment and fermentation	Alkaline pretreatment: 70 °C; 455 mbar; 10 g _{dryBSG} in 100 mL of 0.18 mol _{NaOH} ·L ⁻¹ ; 1 h Fermentation: pH 8.0; 20 °C; 0.67 g _{volatilesolids,substrate} ·g _{volatilesolids,inoculum} ⁻¹ inoculate; 10 d	Amino acids recovery along with 6448.9 ± 328.9 mg·L ⁻¹ of VFA production with 54.0 ± 0.1 of long chain volatile fatty acids	[98]
BSG	Proteins and fibers	Enzymatic hydrolysis and sieving	Enzymatic hydrolysis: pH 8.0; 60 °C; 20 µL _{enzyme} ·g _{BSG} ⁻¹ ; 4 h	Protein fraction: 42.8% (w:w) with 43.7% yield Fiber fraction: 80.4% (w:w) with 56.4% yield	[99]
BSH	Xanthohumol	Deep eutectic solvent extraction	Extraction: 60 °C; BSH:DES 1:50 (w:w); choline chloride:propylene glycol 1:2 (mol:mol); 1 h Antisolvent extraction: water:DES 3:1 (v:w)	2.30 mg·g _{BSH} ⁻¹ of xanthohumol	[100]
BSH	Xanthohumol, terpene derivatives, α- and β-acids	Supercritical fluid extraction	50 °C; 300 bar; 50 kg _{CO2} ·kg _{BSH} ⁻¹	Concentrate of xanthohumol, terpene derivatives, α- and β-acids with 11.4% yield with antibacterial, antiproliferative towards cancer cells	[101]

Table 1. Cont.

By-Product	Target Compounds	Method	Operating Conditions	Outcome	Reference
Trub	Biosurfactant	Bacterial bioconversion	30 °C; 200 rpm; 4.18% (v:v) trub; 6 g·L ⁻¹ yeast extract; 0.8 g·L ⁻¹ peptone; <i>Bacillus subtilis</i> ATCC 6051 inoculate; 72 h	62.74 ± 2.09 mg·L ⁻¹ of surfactin	[102]
Trub	Bitter substances	Cross-flow filtration	Microfiltration in diafiltration mode: 25 °C; 4–5 bar; 0.2 µm PVDF membrane Nanofiltration: 25 °C; 20 bar; 150–300 and 300–500 Da PIP membrane	Concentration of bitters substances: permeation of 81% with microfiltration and retention of 90% with nanofiltration	[11]
BSY	Amino acids, glutathione, protein, and β-glucans	Pulsed electric field assisted extraction, incubation and autolysis	Pulse electric field: 15 kV·cm ⁻¹ ; 39.8 to 159.3 µs Incubation: 25 °C; 24 h Autolysis: pH 7.0; 11 d	Amino acids: 114.91 ± 2.86; glutathione: 7.08 ± 0.64; proteins 187.82 ± 3.75 in mg·g _{dryBSY} ⁻¹ After incubation, β-glucans: 275–300 mg·g _{dryBSY} ⁻¹ ; After autolysis, manose: 1.7–2.2 g·L ⁻¹	[103]
BSY	Bioflocculant	Alkaline hydrolysis	100 °C; 2 mol·L ⁻¹ NaOH; 2 times; 1 h	Fraction with 46% of proteins and 29% of carbohydrates used as bioflocculant: treatment of recalcitrant dyes from textile wastewater	[104]
BSY	Fatty acids	Algal bioproduction with dairy wastewater	Pretreatment: lactase and protease hydrolysis of dairy wastewater and mix with BSY Culture: 28 °C; 400 mg _{dry weight} ·L ⁻¹ <i>Aurantiochytrium mangrovei</i> inoculate; 15.34 g _{glucose} ·L ⁻¹ ; 3.22 g _{BSY} ·L ⁻¹	Biomass production of 3.35 ± 0.08 g·L ⁻¹ ·d ⁻¹ with 38.9 ± 0.88% lipid and 29.8% docosahexaenoic acid of dry weight	[105]
BSY	Fatty acids and sterols	Fungal bioconversion	Incubation: 22–25 °C; 1:30 (v:v) <i>Pleurotus ostreatus</i> inoculate; 5–7 weeks Fruiting: 15 °C, 80–90% relative humidity	Lipids content: 89.5–173.5 µg·g _{biomass} ⁻¹ with high polyunsaturated fatty acid content Phytosterols: 257–416 µg·g _{biomass} ⁻¹	[106]
BSY	Peptides	Autolysis and enzymatic hydrolysis	Autolysis: 70 °C; 5 h Enzymatic hydrolysis: 70 °C; 4% (v:v) enzyme; 4.5 h	Antihypertensive biological activity peptides which can be concentrated by NE; final IC ₅₀ : 75.1 ± 10.5 µg _{protein} ·mL ⁻¹	[107]

Table 1. Cont.

By-Product	Target Compounds	Method	Operating Conditions	Outcome	Reference
BSY	Peptides	Cross-flow filtration	pH 8.0; 50 °C; 5 bar; 30 kDa RC membrane	66% peptide retention with limited fouling	[108]
BSY	Yeast extract	Flash hydrolysis	240 °C; 10% dry yeast:water (<i>w:v</i>); 10 s	Yeast extract: 66.5% carbon, 70.4% nitrogen and 61.0% yeast recovery	[109]
BSY + BSG	Platform chemical—Lactic acid	BSY and BSG co-fermentation	Enzymatic pretreatment: hydrolysis at acid pH, addition of 50 g _{BSY} ·L ⁻¹ Fermentation: pH 6.2; 37 °C; 5% (<i>v:v</i>) of <i>Lactobacillus rhamnosus</i> ATCC 7469 inoculate; 36 h	0.89 g·L ⁻¹ ·h ⁻¹ lactic acid productivity with 89% yield	[110]
BWW	Phenolic compounds	Algal bioproduction	Culture: 23–25 °C; 43.2 μmol _{photons} ·m ⁻² ·s ⁻¹ fluorescent light; <i>Scenedesmus obliquus</i> Subcritical waster extraction: 200 °C; 35 bar; 1000 rpm; 1:10 biomass:water (<i>w:v</i>); 10 min	1.016 ± 0.005 mg _{GAE} ·mL ⁻¹ of total phenolic content including 0.167 ± 0.003 mg _{catechin equivalent} ·mL ⁻¹ of total flavonoids	[51]
BWW	Phenolic compounds	Cross-flow filtration	Ultrafiltration: variable pH; 60 °C; 2.2–2.3 bar; 5 m·s ⁻¹ ; 15 kDa TiO ₂ -ZrO ₂ membrane Nanofiltration: variable pH; 50 °C; 23 bar; 600 L·h ⁻¹ ; 200 Da TFC membrane	Total phenolic content rejection: 8% and 0% during ultrafiltration and 84% and 88% during nanofiltration, for pH 6.5 and 13.5 respectively—mainly flavonoids compounds 0.167 ± 0.003 mg _{catechin equivalent} ·mL ⁻¹ of total flavonoids	[111]
BWW	Phenolic compounds	Cross-flow filtration and ion-exchange process	Ultrafiltration: pH 6.5; 60 °C; 2.3 bar; 5 m·s ⁻¹ ; 15 kDa TiO ₂ -ZrO ₂ membrane Ion-exchange: pH 6.5; 25 °C; 160 rpm; SCAV4 resin with OH ⁻ as counter ion; 50 g _{dryresin} ·L ⁻¹ ; 24 h	Adsorption capacity: 35.4 ± 0.8 mg _{gallicacid equivalent} ·L ⁻¹ (corresponding to 84% of initial phenolic compounds) with a selectivity factor of 5.86 ± 0.97 compared to carbohydrates	[112]
BWW	Platform chemical—Volatile fatty acids	Co-fermentation with cheese whey	pH 6.0; 40 °C; 100 g _{COD} ·L ⁻¹ ; 4 d hydraulic residence time	16 g·L ⁻¹ ·d ⁻¹ of total carboxylic acids with 0.66 g _{CODdigested} ·g _{CODfed} ⁻¹ yield	[113]

Table 1. Cont.

By-Product	Target Compounds	Method	Operating Conditions	Outcome	Reference
BWW	Polyhydroxyalkanoates or related biopolymer	Bacterial bioproduction	30 °C; 200 rpm; <i>Cupriavidus necator</i> inoculate; 5 d	P3HB-co-P3HV copolymer with 2.3 and 0.65 g·L ⁻¹ of P3HB and P3HV respectively	[114]
BWW	Polyhydroxyalkanoates or related biopolymer	Bacterial bioproduction	Fed batch of acidified or anaerobically treated brewery wastewater: 30 °C; microbial mixed culture enriched with PHA accumulating organisms; 105 d	44% (<i>w:w</i>) of PHA accumulated	[115]
BWW	Proteins, carbohydrates and bioactive compounds	Photosynthetic bacterial bioproduction	5–32 °C; 125 W·m ⁻² ; 1.0 g·L ⁻¹ ·d ⁻¹ organic loading rate; 1200 mg·L ⁻¹ inoculate size; 72 h HRT; 440 d	483.5 mg·L _{effluent} ⁻¹ ·d ⁻¹ biomass production with 420.9 protein, 177.6 polysaccharides, 2.53 carotenoid, 10.75 bacteriochlorophyll and 38.6 mg g _{biomass} ⁻¹ coenzyme Q10	[116]

AD: Anaerobic Digestion; BDO: 2,3-Butanediol; BSG: Brewers' Spent Grain; BSH: Brewers' Spent Hop; BSY: Brewers' Spent Yeast; BWW: Brewery Wastewater; DES: Deep Eutectic Solvent; GAE: Gallic Acid Equivalent; IL: Ionic Liquid; PHA: Polyhydroxyalkanoates; PHB: Polyhydroxybutyrate; VFAs: Volatile Fatty Acids.

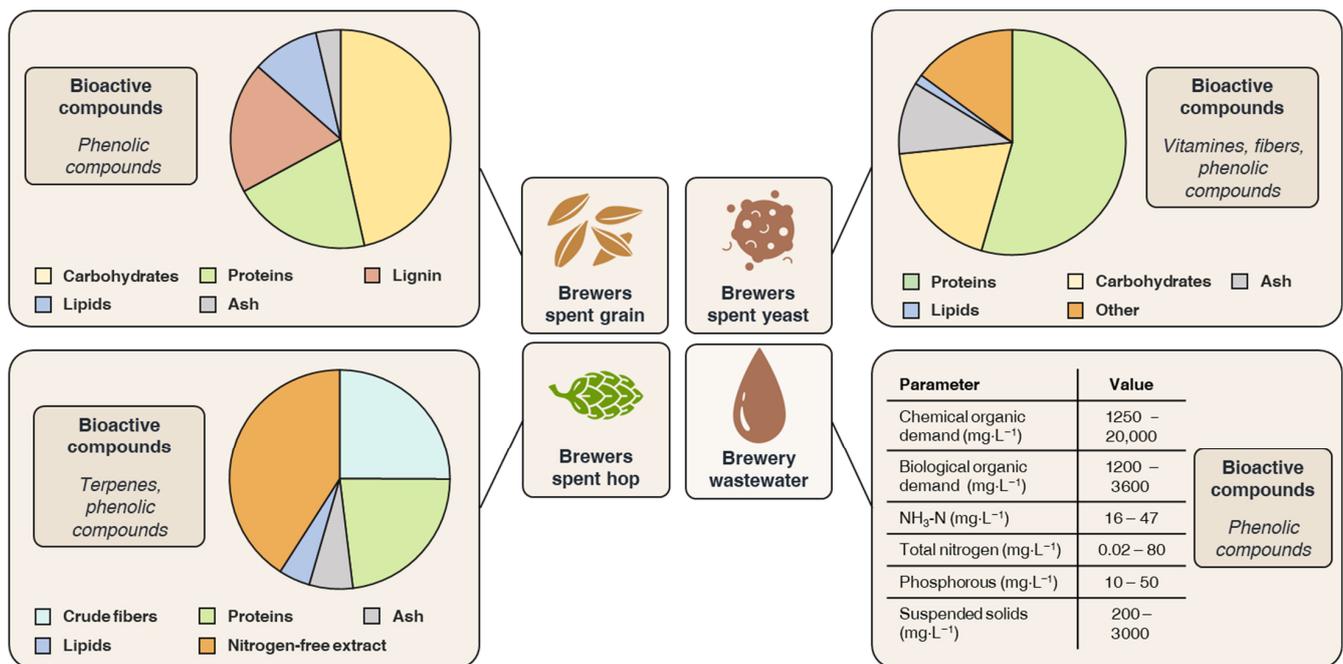


Figure 5. General composition of main brewery by-products: brewers' spent grain [79,80], brewers' spent yeast [81], brewers' spent hop [14], brewery wastewater [13].

5.1. Non-Starch Polysaccharides

Major components of brewery waste matrices are carbohydrate polymers: arabinoxylan, β -glucans, pectin, cellulose, etc. Those constituents are non-starch polysaccharides, also known as resistant starch or dietary fibers. Recovery of these compounds needs depolymerization, which can be realized with commercial or self-produced enzymes [10], or through fermentation. β -glucans are glucose polymers with β -(1-3), β -(1-4) and β -(1-6) linkages, which are primarily present in the BSY cell wall, and are in low proportion in BSG. These chemicals were reported as prebiotic, immunomodulating, antitumoral and antioxidant. These properties allow for the agro-food sector application of β -glucans to develop healthier food [117]; nevertheless, BSY components extraction remains difficult. For example, BSY β -glucan polymers can be fractionated from other compounds with pulsed-field extraction, yielding 275–300 mg·g_{dryBSY}⁻¹ [103].

Arabinoxylan is a major compound of the BSG cell wall, composed of β -(1-4) linkage xylose and pentose. Outeiriño and co-workers focused on the deconstruction of BSG polysaccharides. Solid-state fermentation and the further use of produced enzymes were applied to BSG with the *Aspergillus brasiliensis* strain. The developed procedure yielded $57.04 \pm 2.22\%$ of arabinan, $54.37 \pm 2.34\%$ of xylan, and $24.12 \pm 2.07\%$ of glucan recovery [82]. The separation of non-starch polysaccharides and depolymerization is challenging due to the complexity of plant and yeast matrices. Another strategy is to separate dietary fibers from other compounds, namely proteins and lipids, without further purification of each polymer. Enzymatic hydrolysis and sieving procedures showed protein separation from fibers in BSG with an 84% efficiency, resulting in an 80.8% (*w:w*) fiber fraction with a 56.4% yield [99]. Subcritical water was recently used for the treatment of biopolymer from BSG. This treatment improved extract functionality and gut fermentability, increasing its potential for food and nutraceutical applications [118].

5.2. Proteins and Peptides

Proteins are essential components for biological system construction, function and maintenance. The plant-based diet proved to have lower adverse effects on human health and the environment than meat-based products [73]. Brewery by-products that are rich in protein, such as BSG, BSH, or BSY, can be used as a substitute for the amino

acids found in meats. Furthermore, these protein extracts may have additional bioactive properties, making them attractive for food application. Protein extraction from the brewing industry has been extensively studied in recent years. Another review paper demonstrated that the appropriate pretreatment and development of new methods, such as deep eutectic solvent (DES), microwaves or ultrasound-assisted extraction, improved protein quality and yield [119]. BSG ultrasound-assisted extraction achieved successful protein extraction ($82 \pm 1 \text{ mg}_{\text{protein}} \cdot \text{g}_{\text{dryBSG}}^{-1}$), along with phenolic compounds ($3.28 \pm 0.12 \text{ mg}_{\text{GAE}} \cdot \text{g}_{\text{dryBSG}}^{-1}$) [50]. DES extraction was used on BSH with water antisolvent precipitation. According to the authors, this yielded a fraction with both proteins and xanthohumol, a “dual function” product. A second methanol precipitation followed this to produce a high-content protein fraction (64%) [120]. Naibaho and co-workers investigated the effect of enzyme hydrolysis on the antioxidant capacity and techno-functionality of a protein extract. BSG was treated with and without protease enzymes at pH 8.5 and 50 °C for 3 h, followed by 90 °C heating. Protease treatment enhanced the ORAC and ABTS antioxidant capacity of BSG protein extract and phenolic compounds in the second sediment fraction. The recovered protein fraction with 0.5% protomex contained 37.5% of protein and demonstrated improved techno-functionality with higher oil holding capacity, foaming formation capability and foaming stability and a lower emulsion activity index [121]. BSG proteins were also recovered with alkaline extraction. Changes in operation conditions, namely temperature and pH, were demonstrated to modulate protein content and the techno-functionality of these proteins, with varying solubility, emulsifying and gelling properties [97]. Furthermore, based on a recent study, protein can be extracted from BSG without affecting its fermentative potential for volatile fatty acid (VFA) bioproduction. This dual valorization of protein and VFA maximized the potential revenue (\$37,909.00 per ton of BSG), compared to a VFA-only model (\$258.80 per ton of BSG) [98].

The main source of BSY proteins are mannoproteins, which are glycoproteins and represent 35–40% of cell walls [117]. Mannoproteins appeal to food applications due to bioactive properties, such as angiotensin-converting enzyme-inhibitory (ACE-I) effects [107]. Still, serial repitching seems to be a process that influences BSY characteristics, with increasing protein content and diminishing values of ACE-I and protease activities. Hence, repitching must be considered in the valorization strategy [9]. Mannoproteins can be recovered through hydrolysis processes [107,109]. Level ACE-I activity can be modulated with operating parameters, such as hydrolysis time and enzyme–substrate ratio [107]. The nutritional quality of BSY could also be enhanced with an appropriate fermentation process. The use of *Propionibacterium freudenreichii* improved essential amino acids, vitamin B₁₂, and the short-chain fatty acid content of BSY [122]. Hence, protein properties can be tailored with innovative and versatile technology development to fit food industry applications. The adequate fractionation of proteins with enhanced techno-function and health-benefit properties would ultimately lead to an attractive final product, facilitating valorization.

5.3. Lipids and Fatty Acids

Fatty acids and lipids are recovered from brewery by-products, mainly with bioconversion techniques. As for proteins, the structure and properties of extracted lipids influence their techno-functions and determine industrial application potential [123]. Boukid and co-workers produced an unsaturated fatty acid-rich extract with the fungal fermentation of BSG. The fungal bioconversion process reduced cholesterol compared to the initial matrix. Furthermore, bioactive molecules like ergosterol were present in the extract. With high concentrations of unsaturated fatty acid, low cholesterol and bioactive compounds, the derived product showed potential health-promoting effects [106]. Lipid production capacity from BWW with various algal species during 10 d was investigated. *Chlorella* sp. UTEX1602 showed the best performance with a productivity lipid of $42.5 \text{ mg} \cdot \text{L}^{-1} \cdot \text{d}^{-1}$ and 46.5% dry cell weight [124]. Brewery waste may be used as a nitrogen source for media elaboration with other food waste, as demonstrated with BSG [113] and BWW [105]. A mix of mozzarella-stretching wastewater and BWW was used to investigate the polyun-

saturated fatty acid production during 96 h with microalgae (*Aurantiochytrium mangrovei*), with central composite design optimization. The optimized condition process resulted in $10.14 \text{ g}_{\text{dryweight}} \cdot \text{L}^{-1}$ production with 38.9% lipids and 29.8% docosahexaenoic acid, a polyunsaturated fatty acid [105].

5.4. Phenolic Compounds

Phenolic compounds are specialized metabolites widely found in the vegetal world, which are synthesized for plant defense against oxidation, micro-organisms, etc. [125]. These compounds are in a polymeric form, such as lignin, and can be found bound to plant cell walls or in a free form. Phenolic compounds were extensively studied for their antioxidant effects and related health benefits with action against inflammation [126], tumor [127], cardiovascular and neurodegenerative disorders [128], etc. The clever use of by-product valorization processes likely represents a factor for product quality enhancement. Phenolic compounds were extracted from phenolic-rich solid by-products, especially for BSG with microwave or ultrasound-assisted extraction [88–90]. BSY and BSH phenolic compounds were studied to a lesser extent as these by-products seem to show lower concentrations of phenolic compounds, limiting economically viable extraction process development. Based on an analysis of 20 phenolic compounds using HPLC-ESI-MS/MS, Cortese and co-workers reported a barley husk (BSG) phenolic concentration of $340.0\text{--}969.2 \mu\text{g} \cdot \text{L}^{-1}$; in comparison, the concentrations were $8.0\text{--}22.0$ and $12.5\text{--}56.7 \mu\text{g} \cdot \text{L}^{-1}$ for BSH and BSY, respectively [129]. The recovery of phenolic compounds from BSY and BSH should be integrated with a comprehensive valorization process with other valuable compounds such as nitrogenous compounds, essential oils, etc.

BWW was identified as an attractive medium for the recovery of phenolic compounds, which are mostly flavonoids and display antioxidant, antibacterial and antitumor activity [62]. These compounds can, for instance, be recovered through algal phytoremediation. Ferreira and co-workers grew microalgae in BWW and extracted bioactive compounds with a subcritical water process, i.e., $1.016 \text{ mg}_{\text{GAE}} \cdot \text{mL}^{-1}$ of TPC and $0.167 \text{ mg}_{\text{CE}} \cdot \text{mL}^{-1}$ of total flavonoids. After pyrolysis, algal biomass was also yielded in energy streams, biohydrogen, bio-oil and biogas, and biochar, which can be used as fertilizer [51]. These outputs were identified as valuable products that could sustain the implementation of the subcritical water extraction process. Further research showed that using CO_2 during subcritical water extraction increases the extraction of phenolic compounds to $1.767 \text{ mg}_{\text{GAE}} \cdot \text{mL}^{-1}$ and highlights the microbial safety of extracts [130]. A more efficient strategy may be phenolic compound recovery through a phenolic-rich stream screening. Specific brewery cleaning-in-place residue was identified as a phenolic-rich waste stream [111]. This brewery wastewater was processed with UF and NF as clarification and concentration steps, respectively. Phenolic compounds mostly passed through the UF membrane and were rejected by the NF membrane. Phenolic compounds were retained according to their chemical structure and affinity with membranes. Some phenolic classes, such as flavonoids, were selected among other compounds as single hydroxyl group phenolic acids. Thus, the designed UF/NF process allowed for tuning the NF retentate antioxidant profile. In addition, permeate was an alkaline-clarified water that could be reused for further cleaning in place operations [111].

Various methods have been developed to extract phenolic compounds from brewery waste streams. The suitability of these compounds for specific application fields, such as the pharmaceutical or cosmetic industries, may necessitate their purification, thus requiring further downstream processing. However, in cases where unpurified high antioxidant extracts are expected, such as in the food or material sectors, phenolic compounds obtained from brewery by-products may be applied directly without any additional processing.

5.5. PHA and Related Biopolymers

Plastic has negative environmental impacts. Biopolymers are bio-based materials that are promising alternatives to petroleum-based products, aiming to be biodegradable and

have similar mechanical and physicochemical properties [131]. Polyhydroxyalkanoates (PHA) and related biopolymers, such as poly-3-hydroxybutyrate, are types of polyester that are produced by various microorganisms. These substances are accumulated inside cells when the microorganisms experience a nutrient stress condition, which is typically caused by feast/famine cycles [132]. These microorganisms can grow on synthetic media or carbon-rich by-products, such as food-processing waste streams. Two strategies are commonly used during brewery waste processing: pure culture [95,114] and mixed-microbial culture (MMC) [96,115]. Amini and co-workers produced PHA from BWW with an added carbon source (maltose) with the commonly used *Cupriavidus necator* strain. Operating conditions, especially the nutrient C/N/P ratio, were optimized to modulate the biopolymer production. Indeed, it was demonstrated that an optimal nutrient ratio of 100:2:15 C/N/P led to a high production of PHA, including a Poly(3-hydroxybutyrate)-3-co-(hydroxyvalerate) copolymer [114]. This copolymer seems to possess interesting physicochemical properties, which suggests its application as a packaging material, such as a food packaging film [133].

Biobased plastics can be produced from food waste, including beer production by-products. However, the bottleneck in this technology lies in the downstream processes required to have low- or high-grade biopolymers before their application. The conventional use of organic solvents in these processes decreases their environmental and economic performances. Thankfully, sustainable extraction technologies have been developed recently, such as using surfactants or fusel alcohols, a by-product of ethanol biorefinery, to address these issues [134].

5.6. Other Biomolecules

As an alternative to petroleum-based chemical products, innovation demonstrated that a plant-based equivalent can technically be used as a substitute. However, the cost of such sustainable solutions is often higher than the cost of oil-based solutions. To overcome this limitation, using by-products as a cheap source may be a way forward. The gap between waste stream valorization and green chemistry applications can be filled with platform chemicals, or “building blocks”. Platform chemicals are primary compounds used in chemical and related industries for multiple operations. VFAs are two- to six-carbon fatty acids, which are fermentable to produce PHA or biogas. Due to their chemical function, VFAs are the starting base for the production of various organic compounds, making them essential building blocks. VFAs were produced through biological routes with the fed-batch co-fermentation of cheese whey and BWW, resulting in $30 \text{ g}_{\text{VFA}} \cdot \text{L}^{-1}$ [113]. Short-chain fatty acids produced from BWW can be converted to medium-chain fatty acids with extended fermentation time and biogas production [43]. Lactic acid was recently produced from BSG with a maximum concentration of $59.3 \pm 1.0 \text{ g} \cdot \text{L}^{-1}$ with a simultaneous saccharification and fermentation strategy [94]. Amraoui and co-workers pretreated BSG with a microwave-assisted alkaline process followed by enzymatic hydrolysis. A mutant *Enterobacter ludwigii* strain was grown on BSG hydrolysate, and yielded $118.5 \text{ g} \cdot \text{L}^{-1}$ 2,3-Butanediol with the productivity and yield of $1.65 \text{ g} \cdot \text{L}^{-1} \cdot \text{h}^{-1}$ and $0.43 \text{ g} \cdot \text{g}_{\text{glucose}}^{-1}$, respectively [91]. 2,3-Butanediol and its derivatives have great potential in the cosmetic, agro-food, material and chemical industries [135]. Other platform chemicals were recently produced or extracted from brewery wastes, such as 5-hydroxymethylfurfural [92], itaconate [93], etc. Although bioconversion techniques are adaptable and can produce various compounds, downstream processes for purifying the produced chemicals are rarely investigated. Systems that can simultaneously produce and separate platform chemicals should be developed.

In addition to phenolic compounds, various bioactive and functional compounds were recovered from waste streams. BSH and hot trub seem to be rich sources for biomolecule extraction. Xanthohumol recovery was successfully achieved from BSH with DES extraction [100] and supercritical fluid extraction [101]. Membrane processes were used to fractionate bitter substances, such as lupulones, iso- α -acid and humulones [11]. In addition, glutathione was extracted from BSY at $7.08 \pm 0.64 \text{ mg} \cdot \text{g}_{\text{dryweight}}^{-1}$ with a pulsed electric field, along with proteins and amino acid [103]. BWW bioconversion processes

represent ways to recover bioactive compounds such as carotenoids, chlorophyll or enzymes [105,116,124].

6. By-Product Extract Applications

Researchers recently developed processes to increase the applicability of the beer industry by-products, especially in the food sector. As an example, it has been demonstrated that BSY is a by-product rich in compounds, with potential application in food products [136]. A common use is in the form of BSY-derived products for salads, e.g., yeast powder. Taking advantage of their properties, recovered biomolecules can enhance application matrices' techno-functionality even more than direct application (Figure 4). A salad dressing was prepared with BSY mannoproteins and compared with a dressing formed with soy lecithin. Results showed that the dressing created with BSY exhibited enhanced flavor, color and taste scores after 28 d of storage [137] due to the preservative power of the BSY extract. Reis and co-workers investigated β -glucans and mannoproteins in the formulation of clean-label mayonnaise with the following different extractions from BSY: alkaline hydrolysis with $1\text{--}4\text{ mol}\cdot\text{L}^{-1}$ KOH during 2 h or subcritical water extraction at $200\text{ }^{\circ}\text{C}$ during 2 min using microwaves. These two treatments yielded fractions rich in N-linked and O-linked type mannoproteins, respectively. Mannoprotein conformations conditioned emulsion performances. The BSY extract from the $4\text{ mol}\cdot\text{L}^{-1}$ alkaline hydrolysis procedure was incorporated in a mayonnaise formulation at a 1% (*w:w*) concentration, which resulted in firmness, consistency, cohesiveness and the work of cohesion values of 66, 64, 55 and 51% compared to the standard formulation with 3% egg yolk and modified starch [30]. In another study, mannoproteins and β -glucans extracted from BSY with enzymatic hydrolysis and alkaline/acid hydrolysis, respectively, were added to bread formulation. β -glucan-fortified bread showed 39% higher dietary fiber content, enhancing nutritional value, whereas mannoprotein-fortified bread showed a slight increase in protein but with lower volume [138].

Solid-state fermented BSG was studied for sourdough bread baking. Sourdough bread with 10% fermented BSG scored better in color, structure and taste according to 17 panelists; however, it scored lower in aroma compared to the control, namely bread without BSG [139]. BSG was also valorized in various food products, improving nutritional values of high-fiber content beverages [140] and fish burgers through encapsulation [141]. In order to improve bioactive and nutritive compounds from brewery by-products, further processes, such as extrusion, may be implemented before formulation. The effects of this process on the physicochemical properties of BSG were determined with optimized operating conditions. Extrusion yielded an increase of 61% of soluble dietary fiber, protein quality comparable to egg, soy or milk, lower sugars and digestible starch. It was considered microbiologically safe, making extruded BSG an even more attractive substitution product [142]. The latter was incorporated in the sweet biscuits recipe and commercial fructo-oligosaccharides with respective 17 and 15.2% (*w:w*) ratios. This addition brought multiple nutritional claims, such as reduced sugar reduction, high dietary fiber and protein source, and health improvements, e.g., antioxidant, anti-inflammatory, antidiabetic and promoted intestinal health effects, compared to traditional biscuits [143].

In order to achieve successful applications, some adaptation processes may be needed for some brewing by-products, such as hot trub or BSH, whose bitter characteristics may be restrictive for food products. Hence, debittered trub substituted up to 10% (*w:w*) durum wheat semolina without significant change in organoleptic quality, with fortified protein and a lower glucose content in the final product [144].

Active film packaging prepared from phenolic compounds from brewery waste stream showed increased stability in edible products, with performances similar to those of commercial antioxidants [145]. Recently, a film material was fabricated with BSG arabinoxylans and nanocomposite nanocellulose film. The film demonstrated good mechanical and thermal properties and has been functionalized with feruloylated arabinoxylo-oligosaccharides or ferulic acid. The final packaging material acted as a UV barrier, displaying significant

activity against bacteria and fungi, and represented a promising solution for active packaging [146]. Besides food applications, brewery extracts showed potential in cosmetic industry applications due to their bioactive content. To maximize its biological effects, the optimization of the operating conditions of BSH solid–liquid extraction with water and plant-based propanediol mixture was conducted. The extract showed antioxidant capacity and elastase inhibition effects, mainly due to hop-related compounds, i.e., cis-iso- α -cohumulone and 8-prenylnaringenin [147]. BSG aqueous extract showed skin whitening, tyrosinase inhibition and antioxidant capacity activities [148]. As depicted in Figure 4, the BSY extract may also be used in cosmetic formulations with favorable bioactivity characteristics such as antioxidant capacity, improved mitochondrial activity, keratinocyte oxidative stress prevention, healthy metabolite production enhancement, and with no cytotoxic effects [149,150].

Brewery by-products showed potential applications in various other sectors. A mass of 3 g of BSY was hydrolyzed in a 2 mol·L⁻¹ NaOH solution at 100 °C for 1 h, and the supernatant was tested as flocculants after a 5 min centrifugation at 500 rpm. As a result, 80% to 90% of recalcitrant rhodamine and flavin were removed from synthetic systems, enhancing biodegradability and rhodamine removal from wastewater [104]. In addition to irrigation use, the biostimulant potential of BWW was investigated, like with the microalgae *Scenedesmus obliquus* grown in this waste stream. Downstream-processed biomass yielded biostimulant effects, such as germination or root formation improvement, on watercress seeds, mung bean and cucumber species [151]. Finally, BSG was carbonized in microwaves to prepare carbon dots. This nanoparticle showed excellent optical properties and metal detection capability, with potential in the water treatment and food control sector [152].

Figure 6 presents a controlled and successful brewery by-product valorization process. Brewery by-products can be directly used in various sectors with adequate formulation and application (Section 4). The process of recovering biomolecules through pretreatment and extraction can help the extracts better fit the application. As discussed in Section 5, the nature and operation of the recovery process allow the tuning of the biomolecule composition of brewery by-product extracts. With an appropriate formulation and application development, this tailored chemical composition affects bioactivity and physicochemical properties, ultimately providing a healthy, sustainable and clean label for the final product. This is a crucial step of the valorization process, as it would bring a marketable message that is appealing to the consumer, as highlighted in Section 7.

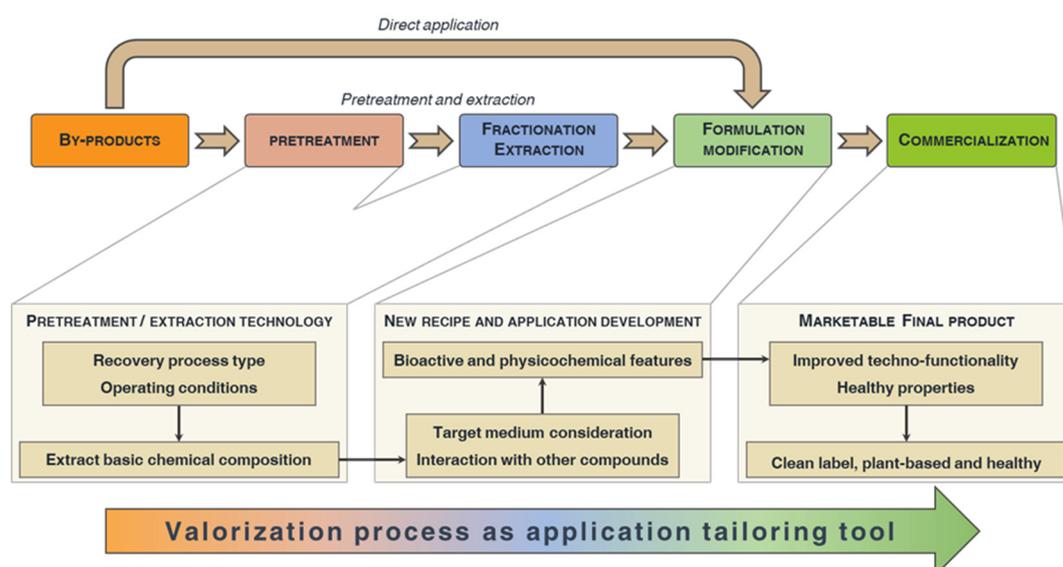


Figure 6. Pretreatment, recovery and application steps enable the modulation of the biomolecule composition of a brewery by-product. The valorization leads to marketable, techno-functional and healthy features of the final product.

7. Strategy for Efficient By-Product Management

7.1. Sustainable Economic Model Implementation Strategies

Sustainable practices in the brewing industry are unlikely to be implemented solely through innovative and efficient process development. When selecting sustainable technologies for brewing businesses, it is critical to consider the economic background of the company. The suitability of a given solution may vary depending on the size of the brewery, ranging from small craft breweries to large industries. In order to transition towards a circular bioeconomy, it is essential to have a thorough understanding of the economic context of the brewing business. To facilitate sustainable practices, Bonato and coworkers developed a new conceptual model for beer production waste management to facilitate sustainable practice based on literature surveys, brewers and expert interviews [8]. This model displayed new BSG valorization possibilities and their integration into craft breweries' value chains. Such a model could be reused for the other types of by-products and help breweries define a sustainable waste management strategy in compliance with their business plans. The authors stated that appropriate organizational adjustment in cultural and operational practices should support this transition [8]. A sustainable path must align with the business background and size to be successfully implemented. Additionally, the sustainability value of by-product processing must be evaluated through tools such as life cycle analysis.

It is important to navigate tensions and tradeoffs among diverse stakeholders in sustainable development to create opportunities for win–win outcomes and synergies [153]. One way to achieve this is through a fruitful waste management strategy that induces shared responsibilities among all actors involved. However, in some cases, implementing a sustainable waste management strategy may not be seen as a win–win situation by all the stakeholders. A recent study established that a collaborative approach to waste management decision-making was necessary for a brewery waste management strategy to be successful [154]. Without a collective effort, the strategy was not seen as beneficial for all parties involved. This collective approach yielded a successful outcome as circular processes between actors emerged to handle brewing waste correctly. The shared-responsibility methodology also enabled stakeholders to see that the benefits of sustainable waste management were not only socio-environmental but also economic [154]. By-product valorization represents additional income for the producer but can also be economically advantageous for the by-product user [155].

7.2. Sustainable Practices as a Marketing Tool

Business images are positively affected by environmentally friendly actions [154]. A sample of 487 online participants was surveyed to investigate water conservation messages' influence on purchase intention. Both craft and industrial beer consumers reacted positively when a company purchased offsets or reclaimed water with a purchase intention raise [156]. In another study, 159 panelists evaluated a cereal bar formed with BSG against one without BSG. Organoleptic and sensory attributes of the BSG bar were scored at a lower level compared to the commercial bar. However, the mention of "rich in fiber" and "produced using byproducts" increased the consumers' purchase intent. As a result, the interference point considered the "normal price" of BSG (1.36 €) as close to the well-known commercial bar (1.41 €), supposedly because of the perception of a BSG bar as a natural product [157]. Developing a sustainable production process contributes to lower environmental impacts of beer production. In addition, it is also likely to enhance the marketing performance of companies, ultimately generating further income.

7.3. Global Strategy for an Environmentally Friendly Brewing Industry

Many valuable compounds can be extracted from brewing industry by-products in a biorefinery concept. The extraction process, formulation and application may modulate extracts' physicochemical, bioactive and techno-functional characteristics and, ultimately, the final product. These by-products are largely under-utilized and may enhance the

social, economic, and environmental performance of the beer sector. A proposed schematic representation of the main findings of the present article is shown in Figure 7.

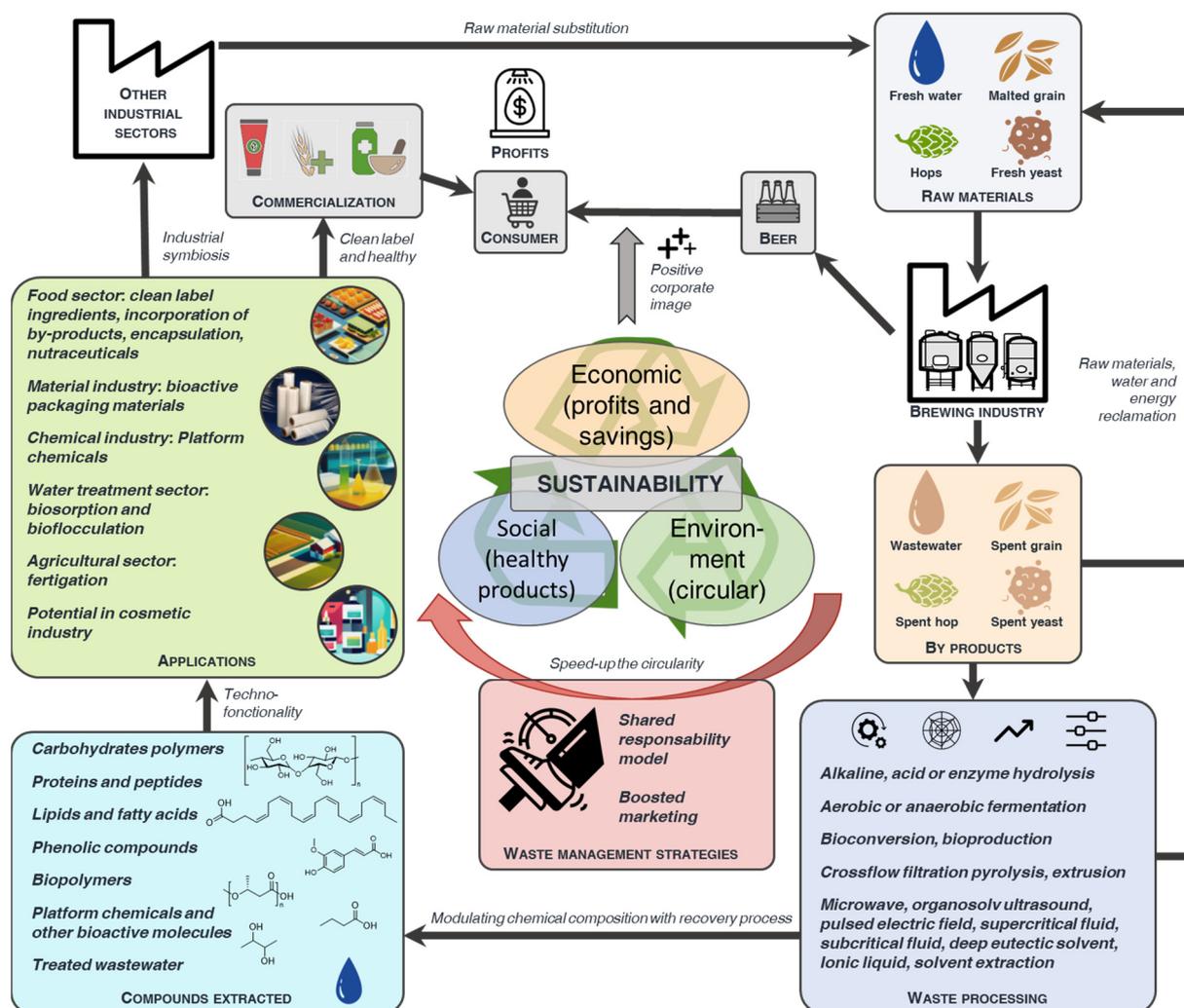


Figure 7. Valorization of brewery by-products for sustainable beer production.

8. Concluding Remarks and Perspectives for Future Research

In order to fit the requirements of a sustainable industrial world needed for environmental transition, the brewing industry can modify its linear production method. Recent research demonstrated the technical feasibility of various processes for reclaiming biomolecules, energy and water. Food, material, cosmetic, agriculture and chemical industries have been highlighted as output sectors for these recovered resources with diverse applications adapted to by-product processing. According to this literature review, environmentally friendly actions lower the corporate footprint, and are also beneficial from an economic point of view.

Some examples of the substitution of raw materials were demonstrated. Ingredient reuse (yeast, bread, hop, etc.) for beer production has been described. However, research on optimizing and modifying brewing processes and recipes is needed to use new raw materials, i.e., residues from other industries or reuse by-products, without altering the final product quality. Responses to water scarcity issues were given in the frame of the brewing industry. The brewing process must be adapted to accept water reclamation with industrial quality, and agricultural research is needed on fertigation with industrial wastewater. Extensive research has been conducted on brewing by-products' bioconversion with microbial or microalgae to produce biomass containing valuable biomolecules, such as carbohydrates,

proteins, lipids, biopolymers (PHA) or phenolic compounds. Downstream processes must be developed to fractionate and extract compounds. A wide range of applications was reported in food sectors, with the ability to modulate the chemical composition and, thus, the physicochemical, techno-function and bioactive properties of the final product through recovery. These direct or indirect applications have been implemented with food and beverage formulations and have shown to be clean-label, healthy, functional and able to supply proteins of plant origin. Brewing by-products have also proven potential in the cosmetic industry, yet there needs to be more formulation and application in real products. In addition, just as studies related to food promote their products using organoleptic tests carried out by panelists, cosmetics studies have to prove that the materials developed with brewing by-products provide healthy properties, are clean-label and attractive to the consumer.

Some technologies were implemented directly in plants as membrane-based systems to reuse water with an evaluation of their economic viability. The emerging technologies developed need scale-up and techno-economic assessment studies to prove their viability. Facing the variety of recovery solutions, life cycle analysis would allow for the evaluation of the environmental performance of each process, and thus, be a decision-making tool development for the design of brewing by-products' valorization strategy. To ensure the sustainability of breweries, a comprehensive waste management approach is necessary. Such plans should involve the recovery, reuse, and valorization of every aspect of by-products, including water, energy, sugar, protein and other bioactive compounds. The primary goal of this approach is to achieve the maximum alignment of valorization processes with conservation, circular bioeconomy, green chemistry and economic viability paradigms. The by-product valorization strategy enables new value chain creation and additional revenue for the producers. More studies are expected on the implantation of circular alternatives, but also on its environmental footprint and financial income impacts on businesses, compared to existing valorization ways.

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